

Density functional calculations of the electronic structure and magnetic properties of the hydrocarbon K₃picene superconductor near the metal-insulator transition

Minjae Kim and B. I. Min*

Department of Physics, PCTP, Pohang University of Science and Technology, Pohang, 790-784, Korea

Geunsik Lee, Hee Jae Kwon, Y. M. Rhee and Ji Hoon Shim*

Department of Chemistry, Pohang University of Science and Technology, Pohang, 790-784, Korea

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We have investigated the electronic structures and magnetic properties of a newly discovered hydrocarbon superconductor, K₃picene, having $T_c=18$ K. We have shown that the metal-insulator transition (MIT) is driven in K₃picene by 5% volume enhancement with the formation of the local magnetic moment. Active bands for the superconductivity near the Fermi level (E_F) have hybridized character of LUMO and LUMO+1 of the picene molecule. Fermi surfaces of K₃picene manifest neither prominent nesting feature nor marked two-dimensional behavior. By estimating the ratio of the Coulomb interaction U and the bandwidth W of the active bands near E_F , we have demonstrated that K₃picene is located in the vicinity of the Mott transition. Our findings suggest that K₃picene is a strongly correlated electron system.

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Recently, the first hydrocarbon superconductivity has been observed in the K-doped picene, K₃picene¹. Its transition temperature $T_c=18$ K is comparable to that of the alkali-metal doped fullerene system ($T_c \sim 38$ K)². In K₃picene, K atoms are intercalated in the stacked picene molecules, as shown in Fig. 1(a). A picene molecule (C₂₂H₁₄) consists of five connected benzene rings with armchair edge (see Fig. 1(b)). Interestingly, alkali metal-doped A₃picenes (A=Na, K, Rb, and Cs) exhibit the cation A-dependent physical properties¹. With increasing the cation size, the system varies from a Pauli-like paramagnet for A=Na to superconductors for A=K and Rb, and then to an insulator for A=Cs. This feature suggests that A₃picene is susceptible to the chemical pressure. This trend is also reminiscent of A₃C₆₀ (A=K, Rb, and Cs), in which changing cation from K to Cs results in 6% volume expansion so as to induce the metal-insulator transition (MIT)³.

Unconventional superconductors often manifest the incipient MIT and magnetic instability, which reflect the existence of strongly correlated electrons^{4,5}. The parent compounds of cuprate high T_c superconductors are typically antiferromagnetic (AFM) insulators⁶. Also the organic superconductors κ -(BEDT-TTF)₂X and A₃C₆₀ (A=K and Cs) show the phase transition from an AFM insulator to a superconductor upon increasing pressure^{2,7}. These examples suggest that investigation of the electronic structures of K₃picene under volume change would provide an important clue to the pairing mechanism of superconductivity.

In this report, we have explored the volume-dependent electronic and magnetic properties of K₃picene using the first principles band structure calculation within the density functional theory. We have shown that the MIT and AFM transitions are driven in K₃picene by 5% volume enhancement with the formation of the local magnetic moment. Our results indicate that K₃picene itself

is on the verge of both MIT and magnetic instability. We have found that the active bands for superconductivity have hybridized character of LUMO and LUMO+1 of the picene molecule. Quantitative estimation of U/W (U :Coulomb interaction, W : band width) also provides that K₃picene is near to the Mott transition.

In the unit cell of K₃picene, there are two stacked picene molecules and six K atoms (see Fig. 1(a)). The positions of K atoms are still undetermined experimentally. Hence, we first optimized the internal atomic positions in K₃picene with retaining the observed monoclinic structure (lattice constants: $a=5.912$, $b=8.707$, $c=12.97$ Å, and $\alpha=92.77^\circ$).¹ For this purpose, we have used the pseudo-potential band method of VASP package⁸. For the exchange-correlation potential, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was utilized⁹. We have used 100 \mathbf{k} -points inside

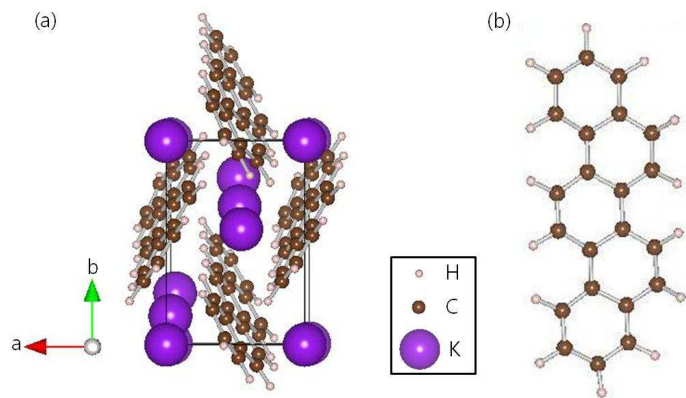


FIG. 1: (Color online) (a) Crystal structure of K₃picene. There are two stacked picene molecules in a unit cell. K atoms are intercalated between the stacked picene molecules. (b) Molecular structure of a picene.

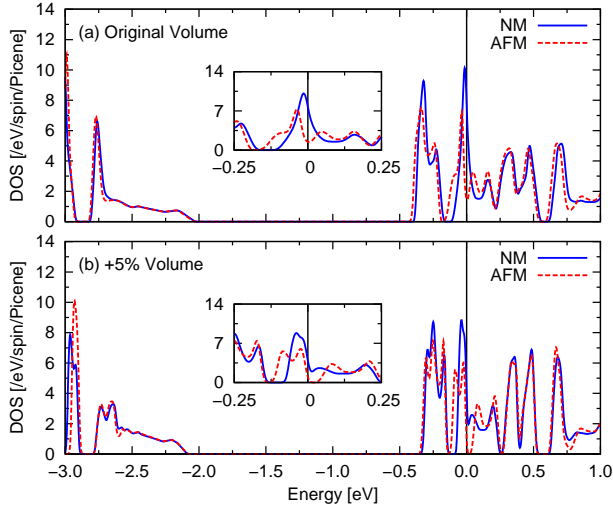


FIG. 2: (Color online) DOS for NM (blue solid lines) and AFM (red dotted lines) phases of K_3 picene. Inset shows the amplified DOS near E_F . (a) K_3 picene with the original volume ($K_3P[OV]$), and (b) K_3 picene with 5% volume expansion ($K_3P[EV]$).

the first Brillouin zone. The convergence of the total energy with respect to number of \mathbf{k} -points was checked to have precision of less than 4 meV per formula unit. For the structural optimization, the atomic relaxations are terminated when the forces in all atomic sites are less than 0.05 eV/Å. The stable positions of K atoms are determined as four above the end benzene rings and two above the center rings with nearly two dimensional stacked arrangement of picene molecules¹⁰, similarly to the results of Ref.^{11,12}. However, the arrangement of picene molecules in Ref.¹¹ are perpendicular to ab plane losing the conventional herringbone structure of the pristine picene solid. Our optimized structure retains the conventional herringbone structure in accordance with Ref.¹². We have also optimized the internal atomic positions of K_3 picene with 5% volume expansion in order to examine the chemical pressure effect, as is realized in Cs_3 picene. Then, based on the optimized structures, we have obtained the electronic structure of K_3 picene by employing the more precise all electron full-potential linearized augmented plane wave (FLAPW) band method¹³ implemented in WIEN2k package¹⁴. To explore the magnetic properties of K_3 picene, we have considered the AFM spin configuration with the opposite spin polarizations of two independent picene molecules in the unit cell.

Figure 2 shows the density of states (DOS) of K_3 picene. DOSs of K_3 picene with original volume (hereafter $K_3P[OV]$) and with +5% volume expansion (hereafter $K_3P[EV]$) are provided in their nonmagnetic (NM) and AFM phases. Pristine solid picene is a semiconductor with a wide band gap of 3.3 eV.¹⁵ Figure 2(a) shows that $K_3P[OV]$ also has an energy gap structure (~ 1.7 eV) between HOMO and LUMO related bands.

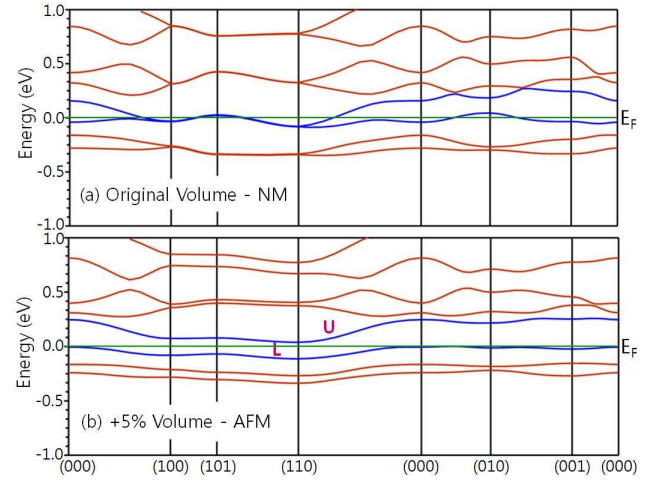


FIG. 3: (Color online) (a) Band structure for NM phase of K_3 picene with original volume ($K_3P[OV]$). (b) Band structure for AFM phase of K_3 picene with 5% volume expansion ($K_3P[EV]$). Notice that two bands near E_F are split into U and L which are represented by blue (dark) color.

In K_3 picene, three electrons are transferred from three intercalated K atoms into one picene, occupying LUMO and LUMO+1 related bands, as was pointed out by Kossugi *et al.*¹¹. For $K_3P[EV]$ in Fig. 2(b), the band widths become narrower to have a larger energy gap (~ 1.9 eV) between HOMO and LUMO related bands. It is seen that, for both $K_3P[OV]$ and $K_3P[EV]$, the DOS at the Fermi level (E_F) is much reduced in the AFM phase with respect to that of the NM phase. Noteworthy is that $K_3P[EV]$ becomes an insulator in the AFM phase, having a small energy gap of ~ 0.03 eV. The NM and AFM phases are almost degenerate. Nevertheless, the magnetic moment of one picene, $\sim 0.35 \mu_B$, is large enough to stabilize the magnetic ground state.^{16,17} These features suggest that K_3 picene ($K_3P[OV]$) is on the verge of the MIT and magnetic instability. The AFM structure in $K_3P[EV]$ with the localized magnetic moment of a picene provides the explanation of the significant enhancement of M/H observed in Cs_3 picene¹. Like other molecular solids (KO_2 , K-doped pentacene, Cs_3C_{60}) having local moment carrying $2p$ electrons^{2,18,19}, the local moment in $K_3P[EV]$ arises from the unpaired electron in the localized molecular orbital.

In Fig. 3(a) and (b), the NM band structure of $K_3P[OV]$ and the AFM band structure of $K_3P[EV]$ are plotted, respectively. The former exhibits a metallic state with two bands crossing E_F , while the latter shows an insulating state. The metallic band structure of $K_3P[OV]$ results from the almost degenerate U and L bands near E_F , while the insulating state in the AFM phase of $K_3P[EV]$ emerges due to the shift up and down of respective U and L bands that had become narrowed due to the volume expansion. Notice that the degenerate bands in the NM phase of $K_3P[OV]$ at \mathbf{k} -points along the (100)-(101)-(110) directions are split in the AFM

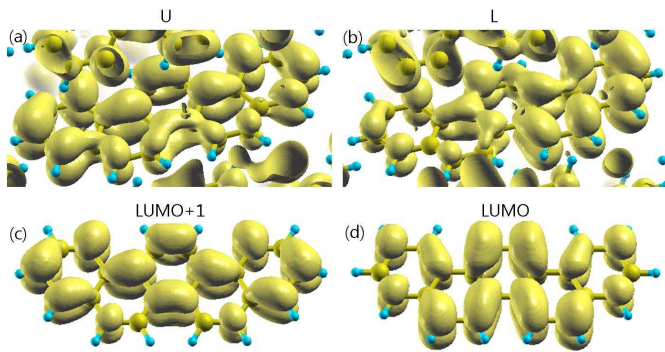


FIG. 4: (Color online) Charge densities (CDs) of (a) U and (b) L bands in Fig. 3. CDs of (c) LUMO+1 and (d) LUMO orbitals of a picene molecule. CD of the U band shows mostly LUMO+1 character with small hybridization with LUMO, while CD of the L band shows hybridized character of LUMO and LUMO+1.

phase of $K_3P[EV]$. The overlap of π - π orbitals of adjacent molecules along the (100) direction produces the symmetric hopping along this direction, resulting in the degeneracy on the (100) zone surface for the NM phases²⁰. This degeneracy on the (100) zone surface is lifted by the AFM spin ordering for both $K_3P[OV]$ and $K_3P[EV]$, due to the broken symmetry along the (100) direction. This feature is reminiscent of the Slater-type MIT mechanism accompanied by the cell doubling, and might suggest that $K_3P[EV]$ can be categorized into a band insulator. However, similar feature was observed in the typical Mott insulating systems such as cuprate and nickel oxides. Therefore, in order to confirm that whether $K_3P[EV]$ is a band or Mott insulator, one needs to check the U/W value of a system, as will be discussed later.

We have examined the orbital characters of U and L bands near E_F that are responsible for superconductivity. The charge densities (CDs) of U and L bands are plotted in Fig. 4(a) and (b), respectively. For comparison, the CDs of LUMO+1 and LUMO of a picene molecule are also provided in Fig. 4(c) and (d), respectively. The CDs in Fig. 4 reveal that U and L bands have the mixed character of both LUMO and LUMO+1, even though LUMO+1 character is dominant for U. The energy splitting between LUMO and LUMO+1 of a picene molecule is known to be 0.15 eV.¹ This gap size is comparable to the band widths of four conduction bands near E_F (U, L, and two lower bands below L in Fig. 3(b)), which correspond to 0.21, 0.12, 0.12, and 0.13 eV, respectively. The comparable size of the gap and band widths indicates that the hybridization interaction between LUMO and LUMO+1 is large enough to yield the hybridized bands with mixed LUMO and LUMO+1 character near E_F . Thus, the active bands for superconductivity near E_F have hybridized character of LUMO and LUMO+1 molecular orbitals, in agreement with the earlier report by Kosugi *et al.*¹¹. This is contrary to the case of pentacene, in which the energy splitting between LUMO

and LUMO+1 (~ 1.28 eV) is much larger than that of picene.¹¹

Fermi surfaces of K_3 picene are provided in Fig. 5. Note first that there is no prominent nesting feature in the Fermi surfaces of $K_3P[OV]$ (Fig. 5(a)), which is in agreement with Ref.¹¹. Secondly, there is no Fermi surfaces of clear cylindrical shape along the c -axis, indicating that this system would not have marked two dimensional behavior, despite its layered-like crystal structure. This feature is indeed consistent with the band structure in Fig. 3(a), which shows apparent dispersions along the c -axis, (100)-(101) and (001)-(000). Figure 5(b) and (c) illustrate explicit effects of AFM spin polarization and volume enhancement on the Fermi surfaces of K_3 picene, respectively. For the AFM phase of $K_3P[OV]$ (Fig. 5(b)), the volume of Fermi surfaces is reduced much, with respect to that of the NM phase of $K_3P[OV]$ (Fig. 5(a)). It is because of the reduced DOS near E_F accompanied by the AFM spin polarization. The volume enhancement also reduces the Fermi surface area, as shown in Fig. 5(c), due to the decreased band width.

We have calculated electrical conductivity σ using the Boltzmann transport theory^{21,22}. The σ/τ (τ : scattering time) value of the NM phase of $K_3P[OV]$ is estimated to be about 0.75 ($10^{19} S/m \cdot sec$). The calculated anisotropy is only about two, which implies that this system is not so anisotropic, as addressed in Fig. 5(a). The reduced Fermi surfaces due to the explicit effects of AFM spin polarization and volume enhancement result in significant drop in the conductivity. The σ/τ values of the AFM phase of $K_3P[OV]$ and the NM phase of $K_3P[EV]$ turn out to be 0.25 and 0.13 ($10^{19} S/m \cdot sec$), respectively, which are only 33% and 17% of that of the NM phase of $K_3P[OV]$ ($0.75 \times 10^{19} S/m \cdot sec$). The conductivity analysis indicates that both volume enhancement and AFM spin polarization are effective for the MIT. The volume enhancement leads to the heavy effective mass in conductivity by reducing W , while the AFM spin polarization leads to the reduced DOS at E_F by splitting two bands around E_F farther.

In general, the volume enhancement of solid decreases the band width W and increases the Coulomb repulsion U , resulting in larger U/W value. The increased U/W , when it becomes larger than the critical value $(U/W)_c$, would drive the MIT through a Mott transition. Indeed, in K_1 pentacene, the formation of insulating state

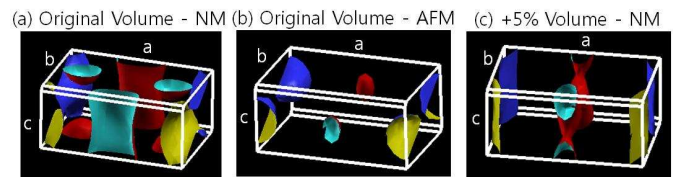


FIG. 5: (Color online) Fermi surfaces of K_3 picene. (a) NM phase of $K_3P[OV]$, (b) AFM phase of $K_3P[OV]$, and (c) NM phase of $K_3P[EV]$.

is experimentally realized²³. We have estimated U/W of K₃picene, using the method of Ref.²⁴ that was applied to the pentacene solid. The effective Coulomb interaction (U_{eff}) is given by subtracting the polarization energy (E_{pol}) from the bare Coulomb interaction (U_{bare}), $U_{eff} = U_{bare} - E_{pol}$. U_{bare} of a charged picene molecule is estimated from the second order Møller-Plesset calculations with 6-31G* atomic orbital basis set for an isolated picene by considering different anionic electron occupations^{25,26}. E_{pol} for a solid K₃picene can be determined by using the partial continuum model, in which a charged molecule is assumed to be surrounded by a cavity of homogeneous dielectric medium²⁴. We have obtained the dielectric constant and the size of the cavity by fitting the calculated E_{pol} to the experimental value of the pristine solid picene²⁷. In this way, we have got $U_{bare} = 2.25$ eV and $E_{pol} = 1.40$ eV, respectively, and thus U_{eff} is estimated to be 0.85 eV. One can estimate the U/W for K₃P[EV] by adopting W of L+U bands near E_F (0.30 eV) for the NM phase of K₃P[EV]. Then we have obtained $U/W = 2.83$, which is larger than $(U/W)_c = 1.73^{28-30}$, so that a Mott insulating state is realized in K₃P[EV]. This large U/W value for K₃P[EV] suggests that K₃P[OV], which exhibits superconductivity, would also be near the boundary of the Mott transition.

In a recent report on the K atom adsorbed picene molecule³¹, it was argued that the charge transfer from K atoms to LUMO and LUMO+1 is not decisive due to the strong Coulomb correlation effect in picene. The above analysis for the Coulomb interaction, however, shows that U_{eff} in K₃picene solid is only about 38% of U_{bare} in an isolated picene molecule. Therefore, distinctly from the case of the picene molecule, the charge transfer from K atoms to LUMO and LUMO+1 related bands will be possible in solid picene due to the reduced

effective Coulomb interaction.

In conclusion, we have studied the electronic structures and magnetism of a first hydrocarbon superconductor, K₃picene, by employing the first principles band structure method within the density functional theory. Active bands for superconductivity are found to have LUMO and LUMO+1 hybridized character. Fermi surfaces of K₃picene manifest neither prominent nesting feature nor marked two-dimensional behavior. The latter is also supported by the rather small anisotropy in the estimated conductivity. We have demonstrated that K₃picene is on the verge of the MIT and the magnetic instability. Therefore, one needs to consider a 3D model with strong Coulomb correlation effects to investigate the mechanism of superconductivity in K₃picene.

After submission of the manuscript, we became aware of a related work by G. Giovannetti and M. Capone, Ref.¹⁷, in which the AFM state is found to become stabilized in K₃P[OV] by the inclusion of correlation effects. Also recent experiment confirms that the Coulomb interaction (U) in solid picene is about 0.85 eV, which is much larger than the band width, Ref.³². These results are consistent with the present results suggesting that K₃picene is a strongly correlated electron system.

Acknowledgments

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* bimin@postech.ac.kr; jhshim@postech.ac.kr

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- in $K_3P[EV]$, the NM and AFM states are nearly degenerate, in view of that the total energy difference is less than the precision of total energy calculation (~ 4 meV). On the other hand, for $K_3P[OV]$, the NM state is more stable than the AFM state by 5 meV per formula unit with similar magnetic moment of $\sim 0.35 \mu_B$ per one picene. The metastable AFM state in $K_3P[OV]$, which has comparable total energy with the NM state, was also reported in Ref.¹⁷ by using the pseudo-potential VASP band method.
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